Source and Chemodynamic Behavior of Diphenyl Sulfone and *ortho*- and *para*-Hydroxybiphenyl in a Small Lake Receiving Discharges from an Adjacent Superfund Site

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Diphenyl sulfone (DPS), *ortho*-hydroxybiphenyl (OPP), and *para*-hydroxybiphenyl (PPP) were found entering a small lake receiving contaminated groundwater discharge from a Superfund Site in Woburn, MA. Concentrations up to 450 μg/L of DPS, 100 μg/L of OPP, and 230 μg/L of PPP were found in the hypolimnion, whereas epilimnetic concentrations of all the chemicals were significantly lower (normally <5 μg/L). The co-occurrence of these compounds, byproducts of the industrial synthesis of phenol, combined with the known historical production of phenol adjacent to the lake strongly indicate that these semivolatiles derived from the manufacturing of phenol. Year-round field studies and laboratory experiments were combined in a mass balance approach to model these pollutants' chemodynamic behavior. All three chemicals were readily biodegradable during warm periods. OPP and PPP showed significant photodegradation rates under sunlight. DPS, OPP, and PPP were of low toxicity and were not mutagenic in human MCL-5 and H1A1V2 cell lines.

Introduction

In an effort to assess the impacts and the environmental fate of organic compounds discharging from hazardous waste sites, we have been examining the inputs of chemicals to Halls Brook Holding Area (HBHA), a small lake receiving groundwater input from an adjacent Superfund Site (Industri-Plex) in the Aberjona Watershed near Boston, MA. Diphenyl sulfone (DPS), *ortho*-hydroxybiphenyl (*ortho*-phenylphenol; OPP), and *para*-hydroxybiphenyl (*para*-phenylphenol; PPP) among other higher phenols were identified by us as some of the major semivolatile organic compounds in the HBHA. Here we report on year-round studies of chemical concentrations, laboratory experiments regarding rates of specific processes, and mass balance calculations to evaluate the fates of these semivolatiles.

DPS, OPP, and PPP are widespread in the environment. They have been detected in rivers, lakes, drinking water supplies, and marine sediments in Europe, the United States, and China (*1–7*). OPP was also found in aerosols (*8*). Despite their widespread occurrence, there are few environmentally relevant data for DPS, OPP, and PPP in the literature. Because of a lack of data, the U.S. EPA recommended in 1991 the

testing of the environmental fate and toxicological effects of sulfones (*7*).

DPS (1,1'-sulfonylbisbenzene) is a known byproduct of the industrial synthesis of benzenesulfonic acids and chlorides (*9*) and is also a known byproduct in the manufacture of phenol. In the past, DPS was applied as an ovicide and acaricide (*9*), but today it is used mainly in the polymer industry (*9*). DPS has low toxicity for rats ($LD_{50,UNR} > 2$ g/kg) and mice ($LD_{50,IVN} > 2$ g/kg) (*10*).

PPP ([1,1'-biphenyl]-4-ol) is an intermediate in the manufacture of resins and in the rubber and printing industries (*9*). Like DPS, it is also a byproduct of phenol manufacture (*11*). Although it is rated as a questionable carcinogen by the International Agency for Research on Cancer (IARC), it has been reported to cause blood tumors (leukemia) when applied orally or subcutaneously to mice (*12*). Soto et al. showed that PPP may be an endocrine disrupter (*13*).

Finally OPP ([1,1'-biphenyl]-2-ol) has the most widespread application today. It is widely used in disinfectant and preservative formulations. It is also used as an ovicide and fungicide in the fruit packing industry and as an intermediate for dyes, resins, and rubbers. This chemical is also known to be produced during phenol manufacture. In addition, it is a product of the photochemical degradation of 2-chlorobiphenyl (*14*). Many studies on its toxicity and mutagenicity have been conducted (for a review, cf. refs *15* and *16*). Although results of experiments in rats provide limited evidence that sodium ortho-phenylate is carcinogenic, other available data are inadequate to evaluate OPP (*16*).

Experimental Section

Description of Field Site. The HBHA is a small, shallow lake in the Aberjona Watershed in Woburn, MA (Figure 1). This lake receives groundwater from the nearby Industri-Plex Superfund Site, a former industrial area with a long history (1853–1967) of manufacture of chemicals (*17*), including acids (H_2SO_4, HNO_3, HCl, acetic acid), dyes and dyestuff intermediates (e.g., H−acid (*18*)), phenolic compounds, lead arsenate pesticides, inorganic sulfur and aluminum salts, tanning materials, and glue (*19–22*). During World War I, large amounts of phenol (*18, 21, 23*), solvents (benzene), explosive intermediates (*24*), and explosives [2,4,6-trinitrophenol (picric acid), 2,4,6-trinitrotoluene (TNT)] were produced (*21*) on the site by the New England Manufacturing Company, an alliance of the Merrimac Chemical Co. and the New England Coke and Gas Co.

The HBHA is a small, elongated, artificial lake (Table 1), created in the early 1970s in place of the former Mishawum Lake for flood control purposes. Its northern end is fed by groundwater springs of high salinity. The surface water receives inflow from Halls Brook and two small drainages in the north of insignificant water input. The outflow empties into an elongated marsh and from there into the Aberjona River (Figure 1). From December 1995 to March 1996, the HBHA was ice-covered with the exception of the most northern and northwestern parts, presumed locations of groundwater inflow.

Sampling and Analysis. In monthly intervals (September 1995–September 1996) water samples for DPS, OPP, and PPP were collected. Lake data were also taken. Temperature and conductivity profiles were measured with a YSI model 33 S−C−T-meter, and dissolved oxygen was analyzed with a YSI 57 oxygen meter, calibrated in pure water equilibrated with atmospheric oxygen. The streamflow rates were determined with a Marsh and McBirney model 201 portable

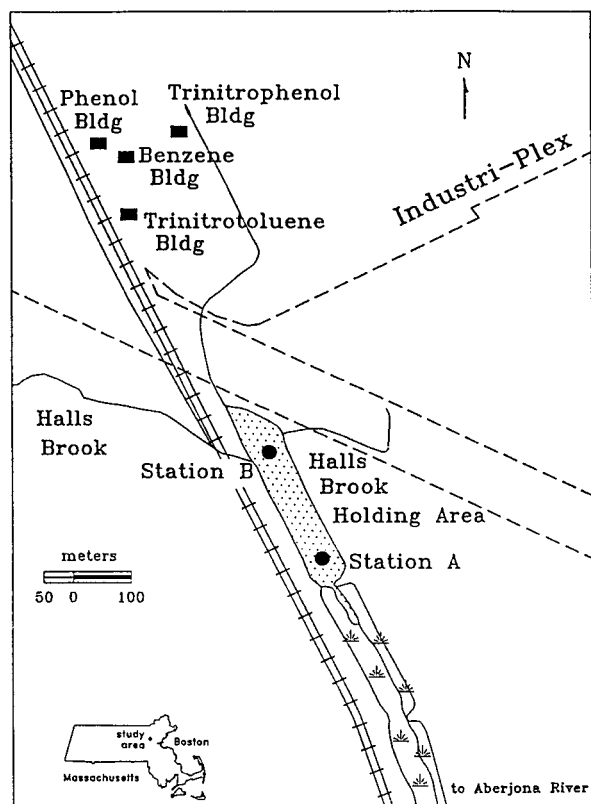* Corresponding author e-mail: pmgschwe@mit.edu; phone: (617) 253−1638.

FIGURE 1. Map of the Halls Brook Holding Area in Woburn, MA; parts of the Industri-Plex Superfund Site; and locations of the manufacture of phenol, benzene, and explosives during WW I. From (57, 58).

water current meter. Water was taken from the epilimnion and the hypolimnion of two locations (Figure 1): station A, at the southern and deep part of the lake (depth: 4.5 m), and station B at the shallower, northern end (depth: 2.2 m). The latter is in an area of expected groundwater inflow. The deep water samples were pumped from approximately 20 cm above the sediment, and surface water samples were taken from about 5–10 cm below the water surface. After collection, the samples were poisoned with dichloromethane (DCM, 60 mL/L) and mercuric chloride (10 mg/L) and stored in the dark at 4 °C until analysis.

Prior to extraction, 100–400 μL of a standard solution of 100 μg/mL para-terphenyl-d_{14} and/or 10–50 μL of para-chloro diphenyl sulfone (520 μg/mL) were added to 1 L of the sample. The water was then extracted with 3 × 100 mL DCM in a 2-L separatory funnel. The combined extracts were run through a drying column filled with anhydrous Na_2SO_4, evaporated in a Kuderna–Danish condenser to ca. 1 mL, then exchanged to n-hexane and evaporated again to 1 mL. Finally 2–10 μL of GC injection standard (anthracene-d_{10}, 500 μg/mL) was added.

A Carlo Erba gas chromatograph (HRGC 4160), equipped with a 30 m, 0.25 μm film thickness, 0.32 mm i.d. DB-5 fused silica capillary column [(5% phenyl)methylpolysiloxane, J&W Scientific, Folsom, CA] was used. H_2 was used as the carrier gas, and the HRGC had an on-column injector and a flame ionization detector (FID). GC–MS was performed on a Hewlett and Packard 5995B (EI, 70 eV) with the same type of column. The unknown compounds were identified by comparisons to GC retention times and mass spectra we obtained for authentic standards. FID response factors were determined using external standards. All data were recovery corrected, using the para-terphenyl-d_{14} and para-chloro diphenyl sulfone as internal standards. Average recoveries

were about 80% (range: 60 to 98%) for epilimnetic and about 55% (range: 30–75%) for the hypolimnetic water. When samples were ran in duplicate or triplicate, the overall precision was about 20%.

OPP (99% (HPLC)), PPP (>99+% (HPLC)), meta-hydroxybiphenyl (MPP) (85%), para-chloro diphenyl sulfone (97%), and 2,2'-dihydroxybiphenyl (2,2'-DHBP) (98%) were used as obtained from Aldrich (Milwaukee, WI). DPS (Aldrich, 97%) was recrystallized twice from methanol prior to use in mutagenicity tests. Diphenylsulfoxide (97%), diphenylsulfide (97%), and diphenyl ether (>98%) were purchased from Fluka (Buchs, Switzerland). para-terphenyl-d_{14} and anthracene-d_{10} were purchased from Ultra Scientific (North Kingston, RI). All solvents were ultra-resi analyzed (J. T. Baker, Philipsburg, NJ). Sodium sulfate (Mallinckrodt, Paris, KY) was Soxhlet extracted for 24 h in a 9:1 methylene chloride/methanol solvent mixture and subsequently activated for 12 h in a muffle furnace at 400 °C prior to use.

Lake water pH was measured using an Orion model SA 720 pH/ISE meter and an Orion combination electrode. Dissolved organic carbon (DOC) samples were filtered through a Millipore AW 19 filter, acidified with phosphoric acid to pH 2, and purged with nitrogen for 5 min prior to analysis. Subsequently, DOC contents were analyzed on a Shimadzu 5000 TOC analyzer. Lake water absorptivity at various wavelengths was measured using 1-cm quartz cuvettes in a Beckman model DU 640 spectrophotometer. Inorganic cations were measured in acidified (5% HNO_3) water samples using a Thermo Jarrell Ash Atom Scan 25 ICP, and anions were assessed using a Dionex ion chromatograph 16 fitted with an Ion Pac AS4A-SC column. Finally, samples with low levels of dissolved oxygen were tested using CHEMets colorimetric procedures (CHEMetrics, Inc., Calverton, VA.)

Biodegradation Experiments. Epilimnetic water was taken 5–10 cm below the surface on 10/24/95 for fall (water temperature, $T = 14$ °C), on 2/29/96 for winter ($T = 5.5$ °C), on 4/28/96 for spring ($T = 13$ °C), and on 8/6/96 for summer conditions ($T = 23$ °C) in a 20-L glass carboy and transported in the dark back to the laboratory. Because of low pollutant concentrations, spring water samples were spiked with OPP and PPP, at about 10 μg/L each. Summer water samples were spiked with 10 μg/L DPS, OPP, and PPP each. For the measurements in the fall and winter, no spikes were added. The water samples were split into chromerge-clean 1-L volumetric flasks, leaving 5 mL volume of headspace in each flask, and capped tightly. Negative controls were poisoned with 10 mg of $HgCl_2$ and 325 mg of NaN_3. The flasks were stored in the dark at the water temperature measured at the time of sample collection. Normally, duplicate flasks were sacrificed at every time point to measure the concentrations of DPS, OPP, and PPP.

On 11/08/95, a biodegradation experiment with anoxic hypolimnetic water (oxygen content < 60 ppb, $T = 12$ °C) was performed. Hypolimnetic water samples were pumped directly into 330-mL BOD bottles, which were allowed to overflow three times their volumes and then sealed airtight with no headspace. To three flasks, 4 mg of $HgCl_2$ and 105 mg of NaN_3 were added before filling them in the field. These flasks were not allowed to overflow. Storage, extraction, and analytical procedures were performed as described above.

Photochemistry Experiments. All photochemistry experiments were performed mainly as described in the literature (25, 26). To assess direct photolysis rates, pure water (reverse osmosis water; Osmonics, Rockland, MA) was used. HBHA water samples were all taken from about 10 cm below the surface, filtered through 1-μm pore size membranes (Nuclepore), and poisoned with $HgCl_2$ (10 mg/L). Briefly, water samples containing DPS, OPP, and PPP were made 2 × 10^{-5} M, placed into 1.3 cm o.d. × 10 cm quartz tubes,

TABLE 1. Characteristic Data of the Halls Brook Holding Area[a]

latitude	42°30′ N	
volume (m^3)	39000[b]	
area		
surface (m^2)	17400[b]	
1.5 m (m^2)	11600[b]	
3 m (m^2)	5990[b]	
4 m (m^2)	2250	
mean depth (m)	2.2	
max depth (m)	4.9	
epilimnion depth (m)	2.5	(0.7−3.7)
winter	2	
spring	3.3	
summer	1.5	
fall	2.3	
residence time of water in epilimnion, $\tau_{w,E}$ (d)	3	(2−120)
residence time of water in hypolimnion, $\tau_{w,H}$ (d)	150	(20−270)
av throughflow of water, $Q_{HB} + Q_{gw}$ (m^3 d^{-1})	9000	(150−19000)
winter	11000	
spring	14000	
summer	2500	
fall	8100	
estimated inflow of groundwater, Q_{gw} (m^3 d^{-1})	100	(40−190)
estimated diffusivity in pycnocline, E_Z (m^2 d^{-1})	0.02−0.07	
dissolved organic carbon (epilimnion; mg/L)	9	(7−11)
dissolved organic carbon (hypolimnion; mg/L)	100	
pH		
surface	6.8−7.1	
bottom	7.1−7.3	
light attenuation coeff		
$\alpha_{300\,nm}$ (m^{-1})	16	(11−24)
$\alpha_{366\,nm}$ (m^{-1})	7	(4−11)

[a] Numbers in parentheses refer to ranges observed in the year-round study. [b] From ref 31.

stoppered, and irradiated in sunlight. Over time, samples were sacrificed to be analyzed and quantified by reverse-phase HPLC [Hewlett and Packard 1050 Series HPLC; Alltech, Adsorbosphere C18 (5 μm) column] with acetonitrile and water (65:35) as solvents. Detection was at 240 (DPS), 245 (OPP), and 254 nm (PPP). Irradiations were performed during July and August 1996 under sunlight, placed on a black, nonreflective background, inclined at about 30° from horizontal with the upper end pointing due north. A correction factor for the geometry of the photoreaction vessel of 2.2 was applied (25). The daily sunlight intensity was calculated as the light intensity for noon conditions divided by 2.5 (25). Solar irradiance data [$W(\lambda)$] as a function of latitude and season were obtained from tables (25). A *para*-nitroac-etophenone/pyridine (PNAP/PYR) actinometer for short term and a *para*-nitroanisole/pyridine (PNA/PYR) actinometer for long-term summer sunlight exposures (25) were used to determine quantum yields (27).

Mutagenicity Tests. DPS, OPP, and PPP were tested for their mutagenic activity at the thymidine kinase (tk) locus in MCL-5 and H1A1V2 cell lines derived from human B-lymphoblastoid cells as described previously (28). All tests were performed by the Gentest Corporation (Woburn, MA). The individual compounds dissolved in DMSO were tested with about 1.8×10^6 cells each. The test concentrations used were 0.01, 0.1, 1.0, and 10 μg/mL for the hydroxybi-phenyls and 0.1, 1.0 and 10 μg/mL for diphenyl sulfone. The mean mutant fraction of each test was compared to the concurrent (Dunnett's t test, $p = 0.05$) and historical negative control observations. Toxicity (survival rates) was deter-mined as the ratio of surviving treated cells to surviving negative control cells measured from the beginning of treatment until plating.

Computer Modeling. Simulation of the month-to-month changes in chemical concentrations in the lake was per-formed using the one-dimensional model CHEMSEE (29, 30). In our model, the water column was discretized into 30 equal-depth vertical compartments. Complete horizontal mixing at each depth and a well-mixed epilimnion (two model assumptions inherent in CHEMSEE) were assumed to be applicable to the situation in the HBHA. Water flows (Q_{HB}, Q_{out}) were set as measured, and epilimnion depth was fixed for each month using measured conductivity profiles. Next, two inputs to CHEMSEE, the inflow of groundwater to the hypolimnion (Q_{gw} holding the conductivity of the ground-water at 4500 $\mu\Omega^{-1}$/cm (31)) and a single vertical eddy diffusion coefficient (E_Z) were adjusted to produce salt fluxes through the lake system such that each month's vertical conductivity profile was matched.

Subsequently, the same parameters ($Q_{Halls Brook}$, Q_{out}, Q_{GW}, and E_Z) were augmented to appropriate input, photochemi-cal, and biochemical degradation rates (Tables 1 and 3). Average groundwater concentrations of 350 μg/L for DPS, 45 μg/L for OPP, and 200 μg/L for PPP however were assumed based on maximal hypolimnion levels. Microbial and photochemical transformation processes were modeled as uniform processes in the whole epilimnion using seasonally varying rate constants (Table 3). All degradation rates were assumed to be of first order and at the rates seen in corresponding laboratory experiments.

Results and Discussion

General Lake Conditions of the HBHA. Due to the very high salinity of the groundwater discharge, the HBHA was stratified year-round (crenogenic meromictic) (Figure 2). Surface water temperatures ranged from freezing to 25 °C, while the deeper water only varied from 7 to 14 °C. The position of the pycnocline (0.7−3.7 m) varied significantly. In the winter when the HBHA was ice-covered and in the summer, epilimnion depths of 1−2 m were observed. During the rest of the year, it was deeper (2.5−3.7 m). A strong conductivity change between epilimnion water with values of 300−600 $\mu\Omega^{-1}$/cm and the hypolimnion water with values of 2500−4500 $\mu\Omega^{-1}$/cm was always seen. This salty hy-
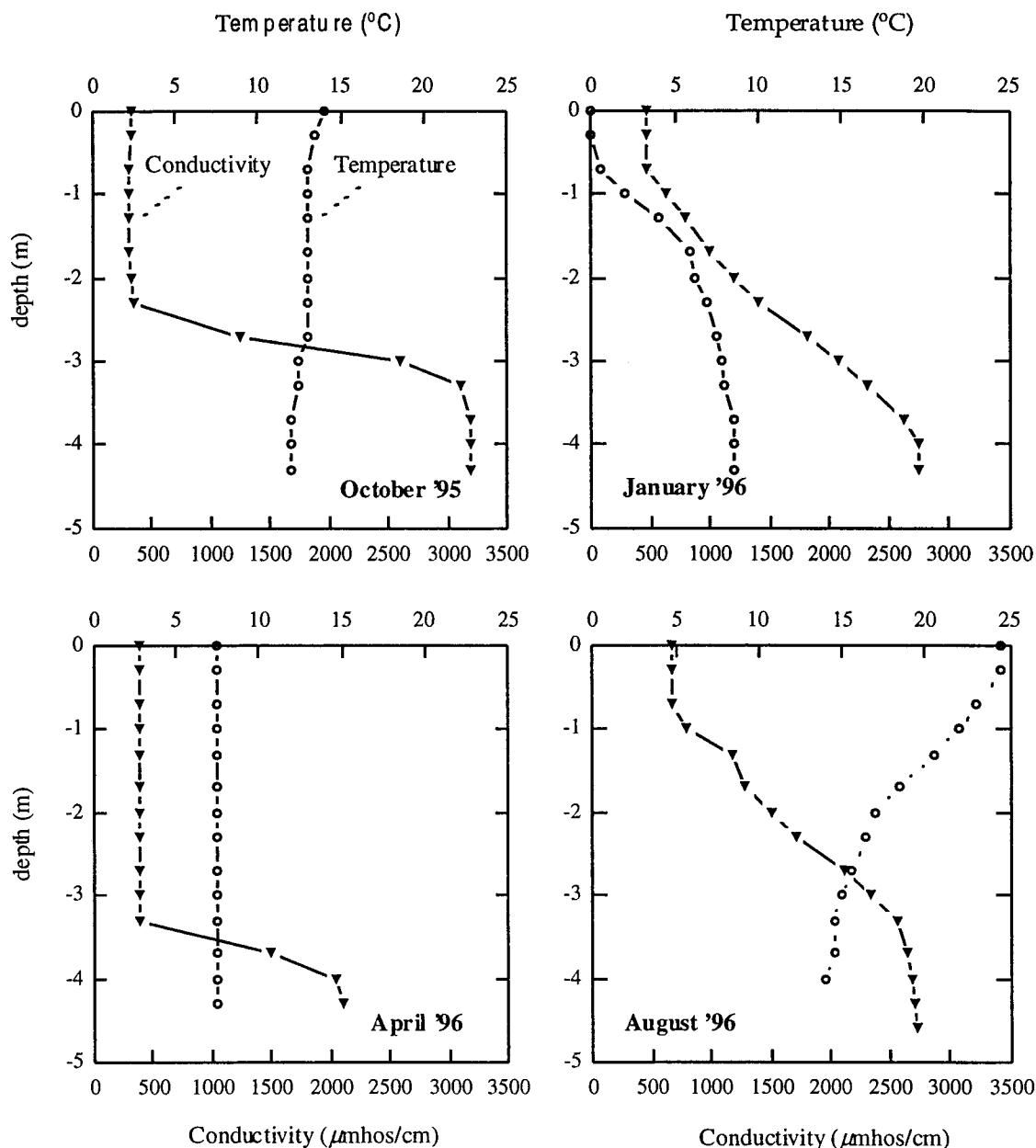
FIGURE 2. Conductivity (▼) and temperature (○) profiles of the HBHA at the deepest point of the HBHA (station A) at different seasons of the year.

polimnetic water was found to have Na^+, Ca^{2+}, SO_4^{2-}, and Cl^- as the major ionic species with concentrations of about 17, 6, 11, and 4 mM, respectively, and an alkalinity of about 1.1 mequiv/L. The conductivity of Halls Brook ranged between 280 and 600 $\mu\Omega^{-1}$/cm. The epilimnion was always oxic, but the hypolimnion was generally anoxic (<1−3 μM).

The HBHA water had high dissolved organic carbon (DOC) and high absorption coefficients ($\alpha(\lambda)$) (Table 1). DOC values ranged from about 9 ppm in the epilimnion to about 100 ppm in the deep water. α (366 nm) ranged from 7 m^{-1} in the epilimnion to 400 m^{-1} in the hypolimnetic water. An average surface water inflow of about 9000 m^3/d through Halls Brook was measured, although this flow varied widely throughout the year. Based on mass balance modeling of the lake water's conductivity, an average groundwater inflow of about 100 m^3/d was estimated. Measurements made by others under low flow conditions (32) found surface and groundwater inputs of 1200 and 20 m^3/d, respectively. The average hydraulic residence time of water in the epilimnion of HBHA was about 3 days, but varied widely (2−120 days)

depending on the season and storm events. The hypolimnion water residence time was typically in the order of 150 days.

Occurrence and Distribution of DPS, OPP, and PPP in the HBHA. Concentrations of DPS, OPP, and PPP were always considerably higher in the hypolimnion than in the epilimnion (Table 2). Higher pollutant concentrations were observed at station B than at station A. This may be due to groundwater inflow in this area. A close correlation between salt content and the concentrations of DPS and PPP was observed. The average year-round ratios between DPS (μg/L):PPP (μg/L):conductivity ($\mu\Omega^{-1}$/cm) were 1:0.6 ($\pm$ 0.1):13 ($\pm$ 3). In the hypolimnion of station A, the concentrations of DPS, PPP, and OPP were 80−320, 50−265, and <0.1−24 μg/L, respectively. DPS showed values in the range of 0.1−13 μg/L for the epilimnion. Significant seasonal variations were observed; for example, highest concentrations in the epilimnion were typically found in the winter, while highest concentrations in the hypolimnion were found in the summer. The concentrations of DPS, OPP, and PPP in the surface water inflow (Halls Brook) were consistently below

	epilimnion					hypolimnion				
	Cond.	DPS	OPP	PPP	MPP	Cond.	DPS	OPP	PPP	MPP
					Station A					
09/26/95	405	9	bd[a]	bd	bd	3400	320	20	260	bd
10/24/95	325	4	bd	bd	bd	3200	220	bd	140	5
11/27/95	330	6	bd	bd	bd	2600	260	bd	150	bd
12/14/95	355	3	bd	bd	bd	2150	130	3	50	bd
01/17/96	470	13	bd	bd	bd	2750	250	20	130	10
02/09/96	340	7	bd	bd	bd	1500	80	bd	60	bd
03/11/96	390	4	bd	bd	bd	2020	170	15	70	bd
04/04/96	390	8	0.3	0.3	bd	2100	250	4	130	bd
05/07/96	390	0.7	bd	bd	bd	2000	220	bd	120	bd
07/25/96	390	bd	bd	bd	bd	2900	160	25	80	8
08/21/96	660	0.6	0.2	0.3	bd	2700	210	25	130	6
09/16/96	550	5	0.4	2.9	0.7	3000	240	30	140	20
					Station B					
09/26/95	395	5	bd	bd	bd	475	13	bd	0.5	bd
10/24/95	325	1	bd	bd	bd	325	9	0.2	0.6	bd
11/27/95	340	6	0.2	1	0.2	380	10	0.2	1	0.1
12/14/96	350	3	bd	bd	bd	3780	170	14	40	9
01/17/96	405	7	0.3	1	bd	1800	350	10	50	5
02/09/96	355	7	bd	1	bd	490	na[b]	na	na	na
03/11/96	395	8	bd	2	bd	445	5	bd	1	bd
04/04/96	385	11	0.5	2	bd	400	14	0.8	4	bd
05/07/96	360	0.1	bd	bd	bd	370	2	bd	bd	bd
07/25/96	385	bd	bd	bd	bd	405	bd	bd	bd	bd
08/21/96	640	1	0.3	1	bd	4500	450	100	230	60
09/16/96	500	1.2	bd	0.7	bd	4650	140	7	40	3

[a] bd, below detection limit of 0.1 μg/L. [b] na, not analyzed.

1 μg/L. Therefore only a small fraction of the entire amount of DPS, OPP, and PPP occurs in the epilimnion, whereas the hypolimnion, despite its smaller volume, is the major reservoir of the three chemicals. The variations of the epilimnion thickness explain the significant changes of the contaminant concentrations and conductivity at the bottom of station B.

Assuming an average groundwater input of ca. 100 m³ per day (with concentrations of 350, 45, and 200 μg/L for DPS, OPP and PPP, respectively) approximately 13 kg/year of DPS and 10 kg/year for the two hydroxybiphenyls entered the lake with the groundwater.

Mutagenicity Tests. There was no evidence of a mutagenic effect of DPS, OPP, and PPP at the tk locus in both cell lines under the conditions of the assay. No response of cultures exposed to any test concentration was significantly different in either comparison to the historical negative controls or in comparison the concurrent negative controls. In addition, all three chemicals were essentially nontoxic to the cells at the concentrations tested. The relative survival rate in both cell lines was in the range of 0.90−0.94 for all chemicals at the highest concentration (10 μg/mL) tested.

Microbial Transformation. Biodegradation of DPS, OPP, and PPP was seen in laboratory systems using aerobic HBHA surface water under spring, summer, and fall conditions. DPS, OPP, and PPP degradation rates were the highest in the summer, whereas no biodegradation was observed during the winter study. Losses in the poisoned control solutions were always negligible (<10%). First-order degradation rate constants were estimated using all the time points, despite the presence of lag periods (Table 3). The lag periods may be due to the spiking of the samples and thus may cause us to underestimate the in situ biodegradation rates. Under the anaerobic conditions in the hypolimnetic water, no biodegradation of DPS and PPP was observed. OPP was not present in the sample studied. However, we suspect that OPP is not significantly biodegraded under anaerobic conditions either.

Photochemical Transformations. 'Near-surface' photochemical transformation rates (k_a^o) (33) were determined under summer sunlight conditions using pure (direct photolysis (25)) and HBHA surface water (direct plus indirect photolysis (25)). The direct photodegradation rates of OPP and PPP observed in pure, oxygen-containing water under summer sunlight were 0.13 and 0.3 d^{-1} and had quantum yields of 0.044 ($s = \pm$ 0.001, $n = 3$) for OPP and 0.098 ($s = \pm$ 0.001, $n = 3$) for PPP, respectively. As expected, DPS showed no direct photolysis (<0.001 d^{-1}), since it absorbs almost no light above 290 nm. In HBHA water DPS, OPP, and PPP however showed direct-plus-indirect photolysis rate constants of 0.005, 0.15, and 0.7 d^{-1}. Taking into account light attenuation in the HBHA water ($\alpha_{(300\ nm)} = 12$ m^{-1}), direct photolysis would account for about 75% of OPP's light-induced removal. In contrast, PPP was degraded only about 40% by direct photochemistry, and DPS was 100% removed by indirect processes. Reactions with light-derived peroxy radicals have previously been reported as important for the degradation of phenols with electron-donating substituents (34).

Due to light scattering and absorption in HBHA water, in situ photochemical degradation rates, however, would be much lower. With typical light attenuation coefficients ($\alpha(\lambda)$) of 16 m^{-1} (300 nm) and 7 m^{-1} (366 nm), 99% of the light entering the surface water is absorbed within the top 10 cm (300 nm) and 24 cm (366 nm), respectively, of the lake. Therefore, in situ photochemical degradation rates (k_a) in the HBHA would be about 100 times slower than we observed in quartz tubes assuming:

$$k_a(\lambda) \sim k_a^o(\lambda)/2.3 D_\lambda \alpha_\lambda z_{mix}$$

with the light distribution function, $D_\lambda = 1.2$ and a well-mixed epilimnion of depth $z_{mix} = 2.5$ m (33). For nonsummer conditions, photochemical processes are even less important due to decreased solar irradiation intensities. To approximate

TABLE 3. Physicochemical Properties (at 20 °C) and Model Parameters for DPS, PPP, and OPP in HBHA Water As Estimated from Literature Data, Laboratory Experiments, and Model Calculations

	DPS	OPP	PPP
mol mass (g mol^{-1})	218	170	170
melting point (°C)	128−129	55.5−57.5	164−165
boiling point (°C)	378−379	280−284	305−308
pK_a	9.97[a]	9.55[b]	
octanol−water partition constant, K_{ow}[c]	250	1230	1590
Henry's law constant, K_H' [d] (mol L$_a^{-1}$/mol L$_w^{-1}$)	8.8×10^{-8}	4.3×10^{-5} [e]	7.7×10^{-6}
air−water transfer velocity, v_{tot}[f] (m d^{-1})	2.4×10^{-8}	1.1×10^{-5}	3.7×10^{-6}
organic carbon−water partition constant, K_{om} [g]	130	480	590
fraction dissolved in water column, f_w[h]	> 0.99	> 0.99	> 0.99
input (hypo), $(Q_{gw}C_{gw})$[i] (kg d^{-1})	0.04	0.005	0.02
input (epi), (kg d^{-1})	0 (?)	0 (?)	0 (?)
characteristic removal constant for			
air−water exchange, f_w (v_{tot}/h)[j] (d^{-1})	10^{-8}	1.7×10^{-5}	1.5×10^{-6}
av flushing of the epilimnion, k_w (d^{-1})			
winter	0.41	0.41	0.41
spring	0.41	0.41	0.41
summer	0.12	0.12	0.12
fall	0.28	0.28	0.28
sedimentation, k_{sed} $(1 - f_w)$[k] (d^{-1})	< 0.01	< 0.01	< 0.01
chemical transformation, $f_w k_{chem}$[l] (d^{-1})	< 0.02	< 0.02	< 0.02
av photochemical transformation, $f_w k_{photo}$ (d^{-1})			
winter[m]	0	0	0
spring[n]	10^{-5}	5×10^{-4}	2.3×10^{-3}
summer	10^{-4}	2×10^{-3}	9×10^{-3}
fall[o]	10^{-5}	3×10^{-4}	1.5×10^{-3}
average biological transformation, $f_w k_{bio}$ (d^{-1})			
winter	< 0.01	< 0.01	< 0.01
spring	0.5	0.3	0.5
summer	2.6	0.7	1.6
fall	0.5	0.3[p]	0.5[p]

[a] From ref 54. Spectroscopically measured. pK_a in water at 23 °C. [b] From ref 55. Spectroscopically measured. pK_a in water at 22.5 °C. [c] From ref 56. [d] C_w(sat) calculated from K_{ow}, using $a = 0.7$ and $b = 1.18$. For P^o(s), $K_F = 1$ (DPS) and 1.15 (PPP) was used (33). [e] K_H' (OPP, 25 °C) is taken from ref 15. [f] Assuming $v_{tot} = v_a'$. Calculated for wind speed $u_{10} = 5$ m s^{-1} with $\alpha = 0.67$ and $\beta = 0.5$. Molecular diffusivities are approximated using molecular weights. From ref 33. [g] K_{om} calculated from K_{ow} (33) using $c = 0.821$ and $d = 0.14$. [h] Calculated for FOM ~ 0.2 mg L^{-1}. [i] Calculated from $Q_{gw} = 100$ m^3 d^{-1}, $C_{gw,DPS} = 350$ μg L^{-1}, $C_{gw,OPP} = 200$ μg L^{-1}, and $C_{gw,PPP} = 45$ μg L^{-1}. [j] Calculated for $h_E = 2.5$ m. [k] Assuming POM = 2 mg L^{-1}, $v_s = 1$ m d^{-1}, mean depth = 3 m. From ref 33. [l] Assuming a decrease of DPS, OPP, and PPP of <10% within 5 days. [m] Assuming no light penetration through ice and snow cover of the HBHA. [n] Average photochemical degradation in the epilimnion. Calculated from W(spring, 40° N, 300 nm) = 0.5 × W(summer, 40° N, 300 nm). Sunlight intensities from ref 25. [o] Average photochemical degradation in the epilimnion. Calculated from W(fall, 40° N, 300 nm) = 0.2 × W(summer, 40° N, 300 nm). Sunlight intensities from ref 25. [p] Estimation from spring data.

photochemical degradation rates for other seasons, summer photodegradation rates were reduced by a factor reflecting diminished light of spring and fall as compared to the summer (Table 3). In the winter, the light penetration through the ice and snow cover of the lake was presumed to be negligible.

Chemical Transformations. No significant chemical degradation (<0.01 d^{-1}) of DPS or the hydroxybiphenyls was seen in poisoned surface samples under light exclusion. Poisoned, anaerobic hypolimnetic water samples also showed no degradation of DPS, OPP, and PPP when kept in the dark for at least 5 days (<0.02 d^{-1}).

Comparison of Field Measurements with Mass Balance Model Predictions. We examined our understanding of the environmental cycling of DPS, OPP, and PPP in the HBHA using a dynamic mass balance approach. For all three compounds sedimentation, chemical and photochemical transformations, and water-to-air exchange were not expected to be important with regard to the mass balance calculations (Table 3). In the winter, flushing acted as a predominant removal mechanism. During the summer, high microbial degradation rates in the epilimnion were most important.

Seasonal variations of the hypolimnetic DPS and PPP concentrations were well predicted assuming no degradation within the hypolimnion (Figure 3). The observed behavior of OPP in the hypolimnion was not consistent with the modeling predictions. Only during four months (January, July, August, September), during which the entire lake was stratified, including the shallow locations with groundwater input, were OPP concentrations predicted appropriately. Under well-mixed and aerobic conditions at the shallower parts of the lake, OPP may undergo an unmodeled degradation processes. Oxidation processes with manganese or iron oxides falling into the hypolimnion from the pycnocline may be responsible for the degradation (35). Colleagues working on the site have observed high loads of iron and manganese in this lake system with typical concentrations of total iron and manganese of 3.5 and 0.05 mM in the hypolimnion and 0.04 and 0.005 mM in the epilimnion, respectively (36).

The epilimnetic concentrations of all three chemicals were not consistent with our estimates based on seasonally varying flushing and biotransformation rates (Table 3; and Figure 3). Except for the summer months, the model consistently underestimated the concentrations of DPS in the epilimnion. During the winter, DPS concentrations were up to 14 times higher than modeled. To resolve the modeling measurement discrepancies, additional DPS sources must be considered. One possibility is a DPS-containing groundwater inflow of low salinity to the epilimnion. On average, an additional input of about 100 m^3/d of DPS-containing groundwater of low conductivity would be needed to match the measured DPS concentrations in the epilimnion. Recently, we have observed groundwater seepage into the epilimnion with low salinity and high DPS concentrations. Alternatively, buoyant mechanisms, such as gas bubble (37) or oil-facilitated, e.g., light nonaqueous phase liquid (LNAPL) transport processes, which carry organic compounds but not salt from the sediment to the epilimnetic layer, were possible. High
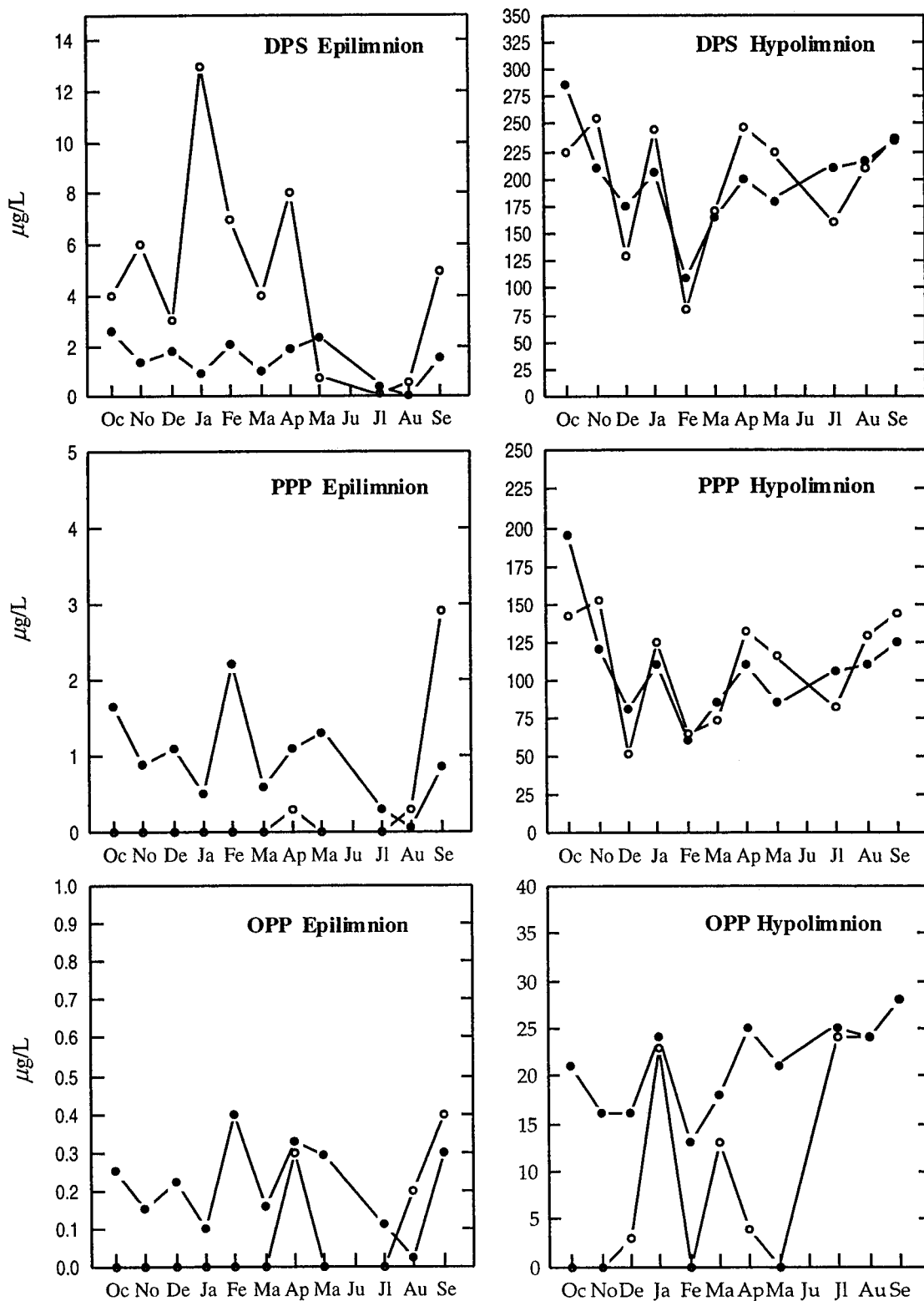
FIGURE 3. Measured (○) and modeled (●) concentrations of DPS, OPP, and PPP for the epilimnion and hypolimnion of the HBHA at different months.

methane and carbon dioxide concentrations were detected in the hypolimnion of the HBHA (38); hence, methanogenesis and microbial respiration may produce enough gas (CH_4, CO_2) to enable bubble release from the sediments. Also we have observed a floating iridescent, oily film on the lake. This film may be enriched in DPS and could have transported DPS from the bed via such buoyant processes. Although all of these processes are likely to be sources of additional DPS,

their quantification is difficult and further work needs to be done.

In contrast, measured concentrations of PPP and OPP in the epilimnion were consistently overestimated by the mass balance model calculations (Figure 3). Additionally, unspecified sink processes with a total rate of about 2 d^{-1} for PPP and 1 d^{-1} for OPP were needed to have model predictions match measured data. We note that by forcing the model
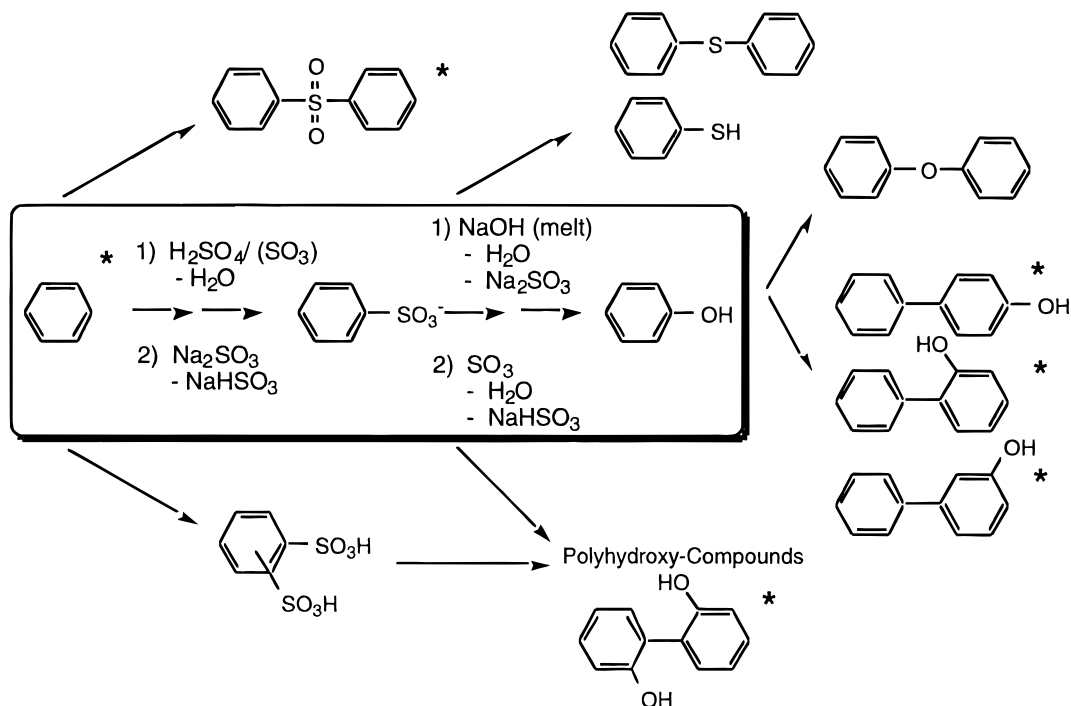
FIGURE 4. Benzenesulfonic acid route to phenol with byproducts reported in the literature (*11, 42, 43, 47, 48*). Compounds with asterisk were identified in the HBHA.

to fit the salt data, we cannot attribute this sink to the flushing of the epilimnion. Although we did not detect chemical degradation of OPP and PPP in poisoned bottles kept in the dark, oxidation processes (*35*) forming quinones and polymeric oxidation products on freshly precipitated iron or manganese oxides at the pycnocline is possible. We also may have substantially underestimated the biotransformation rates of the hydroxybiphenyls with our laboratory biodegradation experiments. In these experiments, water samples were spiked with OPP and PPP concentrations well above those levels normally found in the epilimnion. Typically, we saw lag phases of about 1 day before the rapid phenol degradation. This could indicate that the microbial community had to grow before we could see any significant biodegradation (*39*). Hence our laboratory fits may misrepresent the in situ conditions.

At first glance, one may be dissatisfied since the simulation results appear to disagree with the field observations, especially for the HBHA epilimnion (Figure 3). However, we do not take this to reflect a modeling "failure", but rather this disagreement serves as a diagnostic tool to indicate the nature of problems we still have in a priori chemical fate predictions for the specific environmental system and the compounds we studied. The mismatches here simply indicate the following: (a) there were errors in our assumption that a single contaminated groundwater plume containing constant proportions of salt, DPS, OPP, and PPP was discharging to the lake's hypolimnion; (b) there were problems in using laboratory data to anticipate field processes; and/or (c) we had neglected an important epilimnion degradation process in our conceptualization of the cycles of OPP and PPP. Nonetheless, we can also use the model and data to see that most (>95%) of the mass of each semivolatile that we studied in the HBHA has been well represented by the simple sequence: hypolimnion groundwater input − seasonally variable epilimnetic biodegradation − epilimnetic outflow.

Source of DPS, OPP, and PPP: Manufacture of Phenol. The co-occurrence of DPS, OPP, and PPP in the HBHA led us to seek a common industrial source for them. In light of their chemical structures and the known historical (World War I) production of phenol at the Industri-Plex site, we suspected that they might be related to the production of phenol, a key intermediate of the synthesis of the explosive picric acid. DPS, OPP, and PPP are byproducts (*11, 42, 43*) of the production of phenol via the 'benzene sulfonic acid route'. This manufacturing process was the first large-scale synthesis of an aromatic chemical (*40*) in the United States. It was used in the United States from 1915 until 1978. Briefly, this synthesis consisted of a four-step process (Figure 4) (*41*): (a) sulfonation of benzene with an excess of sulfuric acid, (b) neutralization of the sulfonic acid formed (optional), (c) reaction of the sodium salt or free acid in a NaOH melt at 320−340 °C forming sodium phenolate, and (d) release of phenol by solidification with SO_3. The purification of the crude phenol was performed by a three-stage distillation.

Depending on the sulfonation process used [e.g., the amount of SO_3 present (*44*)], DPS was formed up to 30% of the original benzene processed (*43, 45, 46*). DPS recoveries of modern processes are normally 1−2%. Polysulfonated benzenes and corresponding sulfones were other possible byproducts. In the NaOH-melting process, a variety of phenols (e.g., hydroxybiphenyls, dihydroxybenzenes, dihydroxybiphenyls, etc.) and sometimes the corresponding ethers, benzenethiols, or diphenylsulfides would be formed (*42, 47, 48*). Hydroxybiphenyls are also common byproducts of the chlorobenzene route, another prominent manufacture process to phenol (*41*). A very high yield of inorganic salts (Na_2SO_3 and Na_2SO_4) was also unavoidable using this synthesis, consistent with our observations of Na^+ and SO_4^- as the predominant ions in the lake's hypolimnion. Benzene, one of the key starting materials, was also found in the hypolimnion in concentrations up to 1700 μg/L (*38*). In addition to these compounds, other byproducts of the benzene sulfonic acid route were occasionally seen by us in the HBHA: *meta*-hydroxybiphenyl (MPP), and 2,2′-dihydroxybiphenyl (2,2′-DHBP). Benzenethiol, diphenylsulfide, and diphenyl ether were not detected. Many of our extracted compounds still remain unidentified. In summary, we believe the DPS, OPP, and PPP we found in the HBHA derive

from ca. 1918 chemical manufacturing of phenol.

According to the literature, overall (theoretical) recoveries of the phenol production (sulfonic acid route) varied significantly, depending on the processes used. In 1918, yields normally were between 60 and 75% (typically 90% for the sulfonation and 86−90% for the alkali fusion process) (*47*). In 1935, Mikeska et al. (*11*) examined industrial distillation residues of crude phenol and found approximately 33% DPS, 11% OPP, and 10% PPP as well as tar residues and unidentified phenols. Therefore, per 1000 t of phenol produced, more than 50 t of DPS and 18 t each of PPP and OPP would be expected, assuming only 3% of the initial benzene resulted in DPS and another 3% for the hydroxy-biphenyls.

Starting the manufacture of phenol as early as 1915, The New England Manufacturing Company was one out of five phenol manufacturers in the United States. Within 4 years, the U.S. production of synthetic phenol increased from nothing to over 47 thousand t per year in 1918. Between 1915 and 1919, about 120 thousand tons of mainly synthetic phenol were produced in the United States (*21, 49−52*). No actual phenol production data of The New England Manufacturing Company are available. In 1916, however, this company was one of the major of 20 phenol producers in the United States (*53*). Based on this information, it can be assumed that ca. 2−5% of the total U.S. synthetic phenol production between 1915 and 1919 was produced on this site. This would have resulted in the production of approximately 100−300 t of DPS and 80−210 t of hydroxybi-phenyl waste. If these wastes were dumped at the site, at the current discharges to HBHA (i.e., about 13 kg of DPS and 10 kg of the hydroxybiphenyls per year), a release of these and probably many other unidentified side products could continue for a long time. Similar long-lived problems at other sites can be expected elsewhere where phenol was manufactured.

This discharge of contaminated groundwater to surface waters may affect receptors far from the original disposal site. The hypolimnion of the HBHA acts as a 'reservoir' of the contaminated groundwater inflow from Industri-Plex. This deep water supports a continuous low-level (i.e., ppb) release to downstream locations. It is also possible that during storm events (which we did not monitor) pulses of contamination into the overlaying epilimnion with a subsequent downstream transport occur. Given the none-too-surprising observation, that in the winter when cold water temperatures minimize biodegradation rates, such downstream transport may be especially important at that time of the year.

Acknowledgments

Literature Cited

(1) Waggott, A. *Chem. Water Reuse* **1981**, *2*, 55−59.
(2) Hendriks, A. J.; Maas-Dieppeveen, J. L.; Noordsij, A.; van der Gaag, M. A. *Water Res.* **1994**, *3*, 581−598.
(3) Grifoll, M.; Solanas, A. M.; Bayona, J. M. *Arch. Environ. Contam. Toxicol.* **1990**, *19*, 175−184.
(4) Valls, M.; Bayona, J. M.; Albaiges, J. *Int. J. Environ. Anal. Chem.* **1990**, *39*, 329−348.
(5) Sheldon, L. S.; Hites, R. A. *Environ. Sci. Technol.* **1978**, *12*, 1188−1194.
(6) Jiao, Y.; Sien, S. *Huanjing Kexue* **1988**, *9*, 86−90.
(7) *Fed. Regist.* **1991**, *56* (44), 9534−9572.
(8) Casellas, M.; Fernandez, P.; Bayona, J. M.; Solanas, A. M. *Chemosphere* **1995**, *30*, 725−740.
(9) *The Merck Index*; Budavari, S., Ed.; Merck & Co., Inc.: Rahway, NJ, 1996.
(10) *The Dictionary of Substances and their Effects*; Richardson, M. L., Gangolli, S., Eds.; The Royal Society of Chemistry: Cambridge, U.K., 1992; Vol. 6.
(11) Mikeska, V. J.; Bogert, M. T. *J. Am. Chem. Soc.* **1935**, *57*, 2121−2124.
(12) *Evaluation of Carcinogenic, Teratogenic, and Mutagenic Activities of Selected Pesticides and Industrial Chemicals*; NTIS Report 159, P13-223159; National Cancer Institute: 1968.
(13) Soto, A. M.; Lin, T.-M.; Justicia, H.; Silvia, R. M.; Sonnenschein, C. *Adv. Mod. Environ. Toxicol.* **1992**, *21*, 295−309.
(14) Dullin, D.; Drossman, H.; Mill, T. *Environ. Sci. Technol.* **1986**, *20*, 73−77.
(15) *Dangerous Prop. of Ind. Mater. Rep.* **1994**, *14*, 58−70.
(16) *IARC Monogr. Eval. Carcinog. Risk Chem. Humans* **1983**, *30*, 329−344.
(17) Aurilio, A. C.; Durant, J. L.; Hemond, H. F.; Knox, M. L. *Water, Air, Soil Pollut.* **1994**, *78*, 1−18.
(18) Haynes, W. *American Chemical Industry*; van Nostrand Company Inc.: New York, 1945; Vol. 3, pp 219−220.
(19) Durant, J. L.; Zemach, J. J.; Hemond, H. F. *Civ. Eng. Practice* **1990**, *Fall*, 41−66.
(20) Alder, T. W.; Dougherty, H. M.; Miller, T. T. A Study of the Layout of the Merrimac Chemical Company, Woburn Plant. Master Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1922.
(21) Haynes, W. *Chemical Pioneers*; van Nostrand Company Inc.: New York, 1939; p 71.
(22) Merrimac Chemical Company, Boston, 1928.
(23) Merrimac Chemical Co. U.S. Patent 1245353, 1917.
(24) F. C. Hart Associates *Plan for Investigation of Hazardous Waste Problems: Woburn, Massachusetts Area*; 1980.
(25) Leifer, A. *The Kinetics of Environmental Aquatic Photochemistry*; American Chemical Society Reference Book; ACS: Washington, DC, 1988.
(26) Haag, W.; Hoigné, J. *Environ. Sci. Technol.* **1986**, *20*, 341−348.
(27) Zepp, R. G. *Environ. Sci. Technol.* **1978**, *12*, 327−329.
(28) Busby, W. F. J.; Penman, B. W.; Crespi, C. L. *Mutat. Res.* **1994**, 233−242.
(29) Ulrich, M. Modeling of Chemicals in Lakes−Development and Application of User-Friendly Simulation Software (MASAS & CHEMSEE). Doctoral Thesis No. 9632, Federal Institute of Technology (ETH), Zürich, Switzerland, 1991.
(30) Johnson, C. A.; Ulrich, M.; Sigg, L.; Imboden, D. M. *Limnol. Oceanogr.* **1991**, *36* (7), 1415−1426.
(31) Roux Associates, Inc. Environmental Science & Engineering, Inc., PTI Environmental Services. *Groundwater/Surface-Water Investigation Plan. Phase 2 Remedial Investigation Draft Report. Volume III of III, Appendix D*; Industriplex Site Remedial Trust, 1992.
(32) Davis, A.; Sellstone, C.; Clough, S.; Barrick, R.; Yare, B. *Appl. Geochem.* **1996**, *11*, 409−423.
(33) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; John Wiley & Sons: New York, 1993.
(34) Faust, B. C.; Hoigné, J. *Environ. Sci. Technol.* **1987**, *21*, 957−964.
(35) Stone, A. T. *Environ. Sci. Technol.* **1987**, *21*, 979−988.
(36) Díez, S. Massachusetts Institute of Technology, Cambridge, MA, personal communication.
(37) Martens, C. S.; Klump, J. V. *Geochim. Cosmochim. Acta* **1980**, *44*, 471−490.
(38) Medilanski, E. Massachusetts Institute of Technology, Cambridge, MA, personal communication.
(39) Smith, J. H.; Mabey, W. R.; Bohonos, N.; Hoh, B. R.; Lee, S. S.; Chou, T.-W.; Bomberger, D. C.; Mill, T. *Environmental Pathways of Selected Chemicals in Freshwater Systems. Part II. Laboratory Studies*; Washington, DC, 1978; p 348.
(40) Haynes, W. *American Chemical Industry*; van Nostrand Company Inc.: New York, 1945; Vol. 2, p 22.
(41) Weissermel, K.; Arpe, H.-J. *Industrial Organic Chemistry*, 2nd ed.; Verlag Chemie: Weinheim, New York, Basel, Cambridge, Tokyo, 1993; p 345.

(42) *Ullmanns Encyklopaedie der technischen Chemie*; Urban & Schwarzenberg: München, Berlin, 1962; Vol. 13, pp 424−430.

(43) Stevens, G. H. *Carbolic Acid and its Production from Benzol*; Newark, NJ, 1916.

(44) Guyot, A. *Chim. Ind.* **1919**, *2*, 879/315T-891/327T.

(45) *Ullmann's Encyclopedia of Industrial Chemistry*; Verlag Chemie: Weinheim, Deerfield Beach, FL, 1985; Vol. A3, pp 507−517.

(46) Monsanto Co. U.S. Patent 2889360, 1959.

(47) Peterkin, A. G. *J. Ind. Eng. Chem.* **1918**, *September*, 738−744.

(48) Ney, A. H. *Chem. Trade J. Chem. Eng.* **1915**, *October*, 385−386.

(49) *Angew. Chem.* **1916**, *3*, 393.

(50) Peterkin, A. G. *J. Ind. Eng. Chem.* **1919**, *9*, 475.

(51) Phenol−Report of the United States Tariff Commission to the President of the United States, 1928.

(52) Raschig, F. *Chemiker Ztg.* **1926**, *118*, 1003−1004.

(53) *Weekly Drug Markets* **1916**, *II*, 3.

(54) Beil. 6, *IV*, p 4579.

(55) Beil. 6, *IV*, p 4600.

(56) Hansch, C.; Leo, A.; Hoekman, D. *Exploring QSAR, Hydrophobic, Electronic and Steric Effects*; American Chemical Society: Washington, DC, 1995.

(57) Sandborn Fire Insurance Maps, City of Woburn, MA, 1918.

(58) Darcy, J. Land Use History a Study of Chemical Wastes at one Site in Woburn, Massachusetts. Master Thesis, Bridgewater State College, Bridgewater, MA, 1982.